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A METHOD FOR THE TREATMENT OF WATER-CONTAINING ACRYLAMIDE  
POLYMER

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[There are no amendments to this patent.]

### Claim

A method for the treatment of water-containing acrylamide polymer, characterized in that, in removing unreacted residual monomer from water-containing acrylamide polymer, an organic solvent that selectively dissolves the monomer is added in an amount that is at least 2.5 times the water content in the entire treatment system; the water content in the water-containing acrylamide polymer is adjusted to 5-30% with pulverization of the polymer into small particles and extraction; the polymer separated from the extractant is contacted with fresh solvent with stirring to extract the residual monomer; the extractant is separated, and the polymer is dried.

### Detailed explanation of the invention

The present invention concerns a method for the treatment of water-containing acrylamide polymer, more specifically, concerns a method for removing unreacted monomer from water-containing acrylamide polymer.

Water-soluble polymers of mainly acrylamide are widely used for coagulating agents, thickeners, paper strengthening agents, etc. Such acrylamide-based water-soluble polymers are obtained by polymerizing acrylamide alone or together with one or more of other water-soluble comonomers.

Acrylamide monomer is polymerized often in an aqueous solvent, because water dissolves not only monomers but also polymers well, giving polymers of high molecular weight.

Acrylamide monomers present in polyacrylamide is a toxic substance and may cause skin ailments, paralysis, etc., in actual use, and the government insists on an acrylamide monomer content of 0.05% or less when used as sedimentation agents for tap water. In general, it is self-regulated to 0.2% or less in industry.

For removing unreacted monomer from water-containing acrylamide polymers, the water-containing acrylamide polymer is immersed in an organic solvent that dissolves the monomer but not the polymer for extraction.

However, for this process, it is necessary that the water-containing polymer be immersed in a large amount of organic solvent for a long period, which is an industrial problem.

We have developed a method for efficient removal of unreacted monomer from such water-containing polymer, by a technology comprising three constitutional elements of specifying the water content in the polyacrylamide polymer, specifying the concentration of methanol used, and pulverization in organic solvent. Thus, the present invention is attained.

The organic solvent may be methanol, ethanol, isopropyl alcohol, acetone, etc.

However, for carrying out the operation on an industrial scale, for extracting monomers by simple immersion of water-containing acrylamide polymer in an organic solvent, even when the polymer is immersed in a large amount of organic solvent for a long time, the monomer

removal at the desired level is difficult to achieve, and this is a very difficult chemical operation industrially. On the other hand, recently, the water-containing polymer has been finely divided and then stirred in an organic solvent to shorten the treatment time and enhance removal efficiency. However, even this method requires 2-5 h for residual monomer extraction. Yet, residual monomer removal efficiency is not satisfactory, and this process is not economical.

As a result of an investigation of the methods for efficient removal of unreacted monomer from water-containing acrylamide polymer, we have discovered a method described below for highly efficient removal of residual monomer at an extraction time of less than 30 min.

The water-containing acrylamide polymers used in the present invention may be acrylamide homopolymer, partially hydrolyzed acrylamide polymer, and copolymers of mainly acrylamide and other comonomers. Other copolymerizable monomers include acrylic acid, sodium acrylate, methacrylic acid, acrylonitrile, etc.

In the treatment of the present invention, water-containing acrylamide polymer is pulverized into small particles by a stirrer such as a homogenizer or high-speed cutter such as a juice mixer; then, the polymer and extractant are separated by a filtering machine or a separator such as a centrifugal separator; the separated polymer is immersed in fresh solvent, further stirred and extracted, separated from the extractant and dried for removal of the residual monomer from the polymer. If needed, the stirring and extraction of the polymer separated after the pulverization may be repeated two or three times.

The water-containing acrylamide polymer concentration is desirably 5-30 wt%. At a polymer concentration below 5 wt%, the amount of organic solvent used is excessive, and the pulverized particles may be too fine. Furthermore, extractant separation is very difficult, and the process is very uneconomical. On the other hand, at a polymer concentration above 30 wt%, the pulverized particles are too large with formation of a coating on the particle surface, making residual acrylamide extraction poor with reduced removal efficiency.

In the pulverization-extraction, the amount of organic solvent used should be at least 2.5 times the sum of the water in the water-containing polymer and water in the solvent. At a smaller organic solvent ratio, a portion of polymer is dissolved in the extractant, resulting in reduced polymer yield. Next, the polymer is separated from the organic solvent by a suitable method, then treated with a mixture of at least 85 wt% of organic solvent and water and stirred for further extraction of residual monomer from the separated polymer. The amount of organic solvent used this time should be identical to or smaller than the amount used in the pulverization-extraction step.

Compared with the process involving division of water-containing polymer into fine particles then immersing in an organic solvent for monomer extraction, in the method of this invention, the water-containing polymer is pulverized in an organic solvent; thus, scratches and

cracks are imparted to the pulverized particle surface by the fluid shear force or cutter blade, resulting in a coarse surface. Thus, residual monomer in the water-containing polymer is easily extracted, resulting in increased monomer extraction efficiency.

Next, examples are illustrated.

#### Application Example 1

100 parts of a solution of 10 parts acrylamide in deionized water were prepared and subjected to polymerization by the usual manner to obtain a water-containing polymer. The residual acrylamide monomer was 2% of the total nonvolatile components.

In a sealed pulverizer of inner volume 1 L, 190 g of the water-containing polymer (solids content 10%) in about 3-cm lumps and 500 g pure methanol (2.8 times water) were pulverized at 30°C for 5 min by using a high-speed rotary cutter to particle diameter 3 mm or less. After separation of the extractant and drying, the residual monomer content in the polymer was 0.2% of total nonvolatile components. The separated polymer (water content 42%) was stirred in 250 g of 90 wt% methanol-water (29 times water) at 40°C for 20 min, for extraction, separated from the extractant, and dried to obtain a polymer with residual monomer content of 0.02% of the total nonvolatile components.

#### Comparative Example 1

190 g of the water-containing polymer of Application Example 1 was finely divided to particle diameter of about 3 mm, stirred in 500 g pure methanol at 30°C for 2 h for monomer extraction, separated from the extractant, further stirred in 500 g (2 times Application Example 1) of fresh 90 wt% methanol-water at 40°C for 1 h, freed from the extractant, and dried to give a polymer with residual monomer content of 0.1% of the total nonvolatile components.

Comparison of Application Example 1 and Comparative Example 1 shows that residual acrylamide content is 5 times higher in the comparative example, while the amount of solvent used is 750 g in the application example and 1000 g in the comparative example.

#### Application Example 2

A solution of 85 parts acrylamide, 15 parts sodium acrylate and 667 parts deionized water was subjected to polymerization in the usual manner to obtain water-containing polymer (solids content 15%) with residual acrylamide monomer content of 1.8% of the total nonvolatile components.

In a sealed pulverizer of inner volume 1 L, 140 g of the water-containing polymer in about 3-cm lumps and 530 g of 95 wt% methanol-water (4.5 times water) were pulverized at 40°C for 5 min by using a high-speed rotary cutter to a particle diameter of 3 mm or less. After

separation of the extractant and drying, the residual monomer content in the polymer was 0.1% of the total nonvolatile components. The separated polymer (water content 45%) was stirred in 530 g of 95 wt% methanol-water (56 times water) at 40°C for 20 min, for extraction, separated from the extractant, and dried to obtain a polymer with a residual monomer content of 0.006% of the total nonvolatile components.

### Comparative Example 2

140 g of the water-containing polymer of Application Example 2 were finely divided into a particle diameter of about 3 mm, stirred in 800 g (1.4 times Application Example 2) of 95 wt% methanol-water at 40°C for 2 h for monomer extraction, separated from the extractant, further stirred in 800 g (1.5 times Application Example 2) of fresh 95 wt% methanol-water at 40°C for 1 h, freed from the extractant, and dried to give a polymer with residual monomer content of 0.08% of the total nonvolatile components.

Comparison of Application Example 2 and Comparative Example 2 shows that with no pulverization in the copolymerization of acrylamide and sodium acrylate, the residual monomer content is 0.08%, that is, 13 times. The amount of methanol used is about 1.5 times in both the first and second time, resulting in high residual monomer content.

### Comparative Example 3

100 parts of solution of 4 and 35 parts of acrylamide in deionized water were subjected to polymerization similarly as in Application Example 1 to obtain water-containing polymer with residual acrylamide monomer content of 2% of the total nonvolatile components.

After pulverization similarly as in the application example, in the 4% case, the polymer was microparticulate or fibrillar, making industrial operation difficult.

In the 35% case, the particle diameter was 2-5 mm. The particles were stirred in 500 g of fresh 90 wt% methanol-water at 40°C for 1 h for extraction, separated from the extractant, and dried to give a polymer of residual monomer content of 0.4% of the total nonvolatile components and particle diameter 2-5 mm. It seemed that coating was formed on the particle surface, making extraction of acrylamide monomers inside the particles difficult.

In the comparative examples, in the case of acrylamide polymer with water content beyond the 5-30% range, even with pulverization, the desired products cannot be obtained.

### Comparative Example 4

In a sealed pulverizer, 190 g of water-containing polymer in lumps of about 3 cm per side obtained similarly as in Application Example 1 and 360 g methanol (2 times the water content) were pulverized using a high-speed rotary cutter at 30°C for 5 min. The pulverizate was not

particulate and was in the form of a turbid solution in the extractant. This example confirmed that when the amount of methanol used is not at least 2.5 times the total water content in the pulverization system, pulverization into particulate form is not possible.